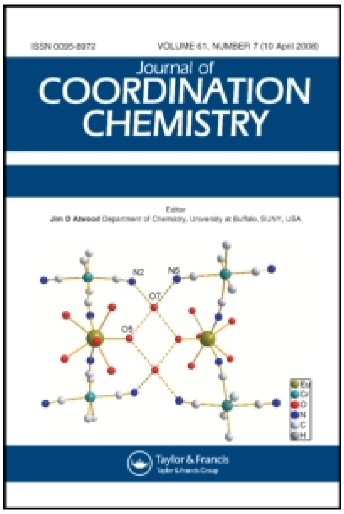

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THE STRUCTURAL AND MAGNETIC CHARACTERIZATION OF THE BINUCLEAR CHROMIUM COMPLEX DI-μ-HYDROXOTETRAGLYCINATODICHROMIUM(III)

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The binuclear complex $[Cr(gly)_2OH]_2$, where gly = $NH_4C_2O_2^-$, has been the subject of much interest since its initial report by Ley and Ficken[3] in 1912. Earnshaw and Lewis[4] have reported the magnetic susceptibility variation for the complex in the temperature range 306–80°K, and although the maximum in susceptibility occurs below the lower limit of this range they were able to conclude from fitting procedures that an antiferromagnetic interaction existed and that the value of 2J (the singlet-triplet splitting) is $-8 cm^{-1}$.

From our recent crystallographic and magnetic studies[5–8] of di-hydroxo bridged complexes of the type $[CuL(OH)]_2^{2+}$, we have been able to conclude that the value of 2J decreases in these systems as the value of ϕ, the Cu-O-Cu bridging angle, increases, and we have explained this phenomenon in terms of the principles of super-exchange.[9] It is also apparent from our studies that the interaction changes from ferromagnetic to antiferromagnetic at a bridging angle between 96° and 99°. Hence, it was of great interest to us to undertake a complete structural and magnetic investigation of this reportedly di-hydroxo bridged chromium complex in order to test the generality of our hypothesis concerning the mechanism of the spin exchange in these systems. We here report preliminary structural data and the low temperature magnetic susceptibility and room temperature EPR spectrum of this compound. A detailed structural report will be published later.

The material crystallizes in the monoclinic space group $P2_1/n$ with two dimeric formula units in a cell of dimensions $a = 5.691(3)$, $b = 16.920(9)$, $c = 7.900(4)$Å and $\beta = 79.90(3)°$. The structure was solved by conventional methods using data collected on an automatic diffractometer with Mo Kα radiation, and has been refined to a conventional R-factor (on F) of 0.039 for 775 data whose intensities were greater than twice their estimated standard deviations. A view of the structure is shown in the figure, and it is apparent that the coordination around the chromium atoms is roughly octahedral.

The Cr—O—Cr—O unit is strictly planar, there being an inversion center in the middle of the dimer, and the Cr—Cr and O—O separations are 2.974(2) and 2.575(6) Å, respectively. Hence, the bridging geometry is similar to that found in $[Cu(bipy)OH]_2(NO_3)_2$ (bipy = 2,2′-bipyridine)[10], $[Cu(EAEP)OH]_2^{2+}$ (EAEP = 2-(2-ethylaminoethyl)pyridine),[7] and $[Cu(tmen)OH]_2^{2+}$ (tmen = tetramethylethylenediamine),[11] in which the Cu–Cu distances are 2.847, 2.917(5), and 3.000(4) Å, respectively, and the bridging moiety is roughly planar. The two independent bridging Cr–O separations of 1.966(4) and 1.968(4) Å are essentially similar. The Cr–O–Cr angle in the bridge is 98.2(2)° while the O–Cr–O angle is (necessarily) 81.8(2)°. All hydrogen atoms were included in the structure refinement, and there is little evidence for hydrogen bonding involving the bridging ligands. The geometry of the glycinato ligands is similar to that found[12] in $Cr(gly)_3.H_2O$. It is also evident from the structure analysis that the complex should be formulated as an anhydrous material and that its formulation as a monohydrate by previous workers[3,4] is presumably incorrect. This conclusion is also consistent with routine chemical analysis.

The magnetic susceptibility of a powdered sample of the complex was measured from 4.2 to 100°K using a Foner-type vibrating sample magnetometer calibrated with $HgCo(NCS)_4$. Tem-

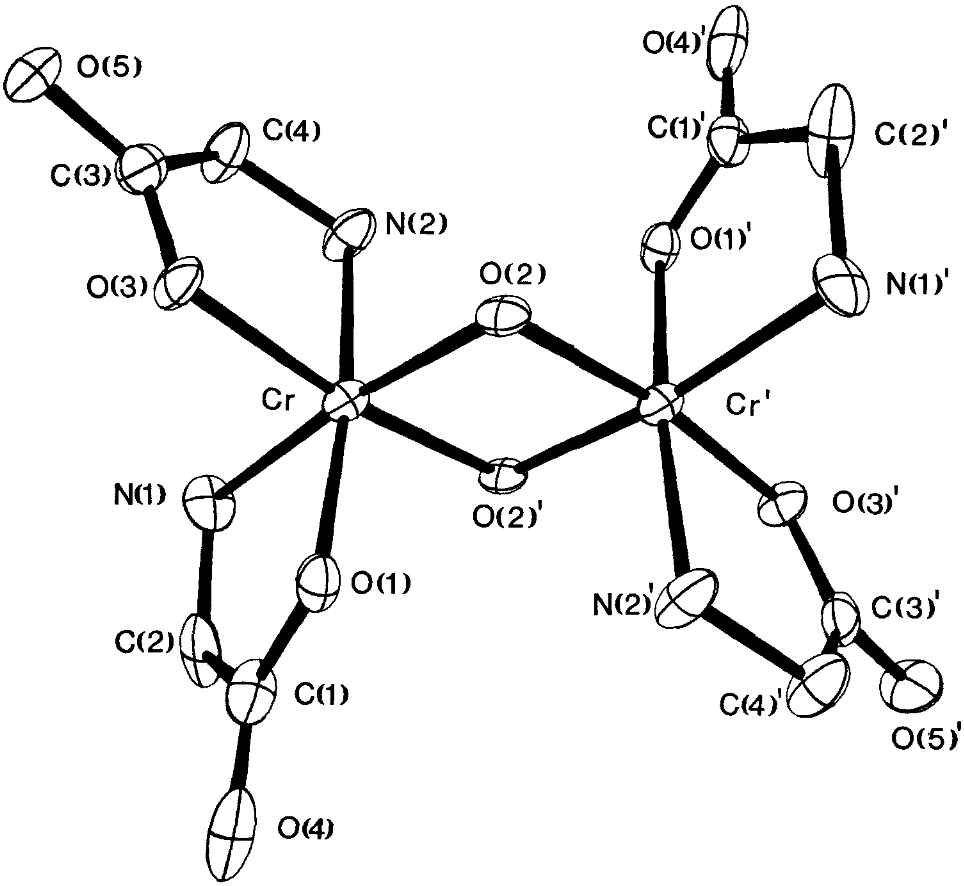

FIGURE 1 View of the complex $[Cr(gly)_2OH]_2$, with hydrogen atoms omitted for clarity.

peratures were measured with a calibrated precision germanium resistor and a high impedance AC resistance bridge. There is a maximum in the magnetic susceptibility at approximately 20°K, and the data may be described by the Van Vleck expression[4] for exchange coupled Cr(III) ions ($S = 3/2, 3/2$) with the parameters $2J = -8.4\ \text{cm}^{-1}$ and $g = 1.95$. These low temperature data may be extrapolated smoothly into the high temperature data reported by Earnshaw and Lewis.[4]

The room temperature X-band EPR spectrum of a powdered sample of the complex consists of a broad, symmetrical resonance centered at approximately $g = 2$. This observation is consistent with the assumption that the Zeeman interaction dominates the zero-field splitting. Using the expression $2D \approx -g\beta(\Delta H)$, where ΔH is the observed line width, we calculate $D \approx 0.074\ \text{cm}^{-1}$.

The values of ϕ and $2J$ found here are in excellent agreement with predictions based on our earlier hypothesis, since both values are intermediate between those found for $[Cu(bipy)OH]_2{}^{2+}$ and $[Cu(EAEP)OH]_2{}^{2+}$; hence, it remains true that for all completely characterized magnetically condensed di-μ-hydroxo complexes the value of J decreases as ϕ increases.

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REFERENCES

1. Tennessee Eastman Corporation Fellow, 1971-72.
2. NSF Trainee, 1968-71.
3. H. Ley and K. Ficken, *Ber.* **45**, 377(1912).
4. A. Earnshaw and J. Lewis, *J. Chem. Soc.* 396 (1961).

5. J. A. Barnes, W. E. Hatfield, and D. J. Hodgson, *Chem. Commun.* 1593 (1970).
6. J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.* **11,** 144 (1972).
7. D. L. Lewis, W. E. Hatfield, and D. J. Hodgson, *Inorg. Chem.*, in press.
8. D. Y. Jeter, D. L. Lewis, J. C. Hempel, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, in press.
9. J. B. Goodenough, "Magnetism and the Chemical Bond", Interscience Publishers, New York, pp. 180 ff., 1963.
10. R. J. Majeste and E. A. Meyers, *J. Phys. Chem.* **74,** 3497 (1970).
11. T. P. Mitchell, W. H. Bernard, and J. R. Wasson, *Acta Cryst.* **B26,** 2096 (1970).
12. R. F. Bryan, P. T. Greene, P. F. Stokely, and E. W. Wilson, Jr., *Inorg. Chem.* **10,** 1468 (1971).